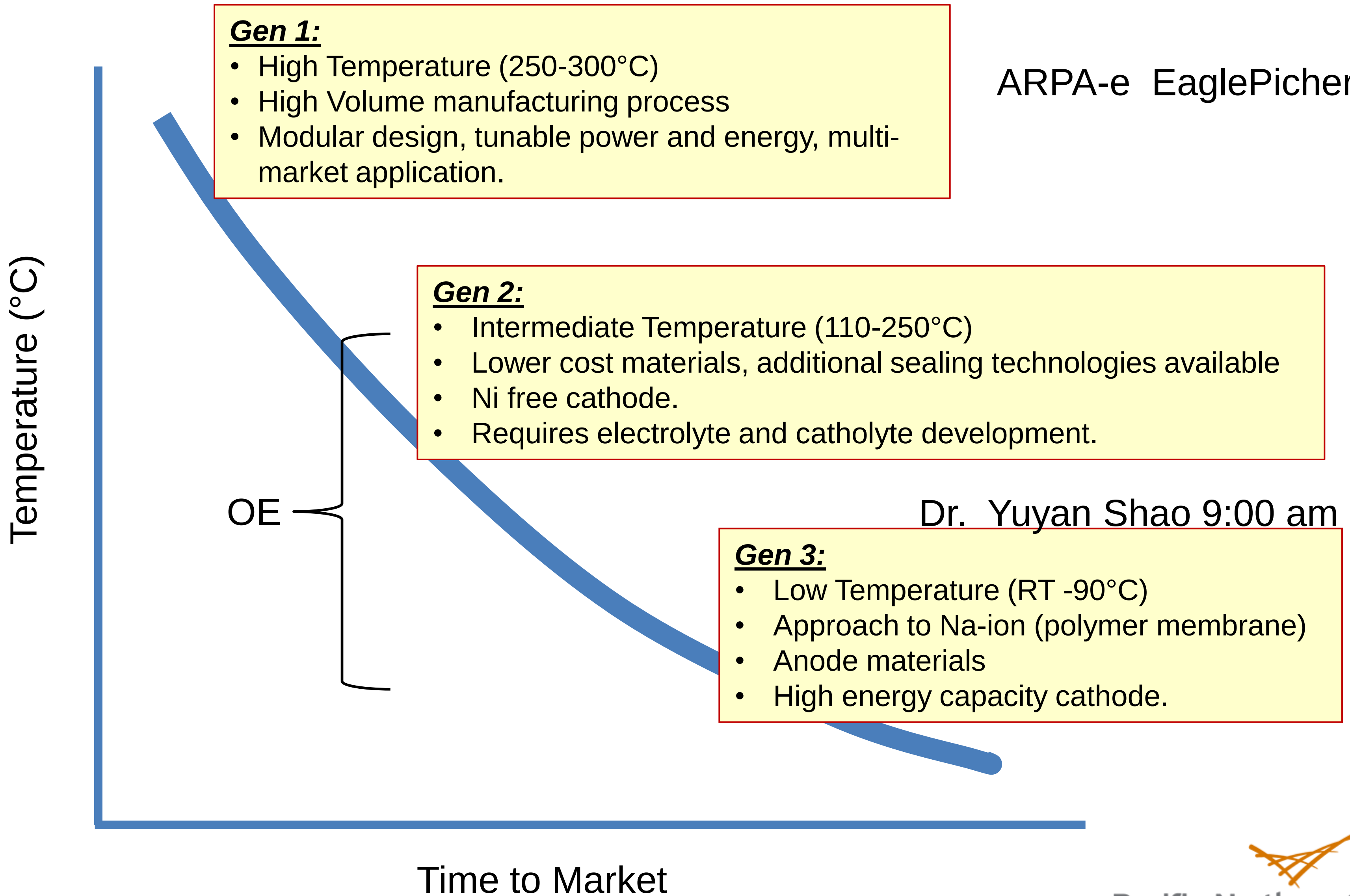
Na-Battery Development at PNNL

- Vincent Sprenkle, John Lemmon, Xiaochuan Lu, Guosheng Li, Jun Cui, Jin Yong Kim, Brent Kirby, Nathan Canfield, Dave Reed, Eric Mast, Richard Pearson, Kerry Meinhardt, Jeff Bonnett, Greg Coffey, Jirgal Mansonav.

- EaglePicher ARPA-e team: Dave Lucero, Bob Higgins, Jim DeGruson, Julie Baumann, Eric Raub, Rebecca Cragan, Charlie Huddleston.

Pacific Northwest NATIONAL LABORATORY

Progression of Planar Sodium Battery Technology



Pacific Northwest NATIONAL LABORATORY

Acknowledgements

- **ARPA-e DOE Award Number: DE-AR0000045**
  - *Dr. Mark Johnson, Dr. Dave Danielson*
- **DOE-OE Energy Storage Program,**
  - *Dr. Imre Gyuk*
- **PNNL internal LDRD Funding**

Pacific Northwest
NATIONAL LABORATORY

EaglePicher Technologies- PNNL

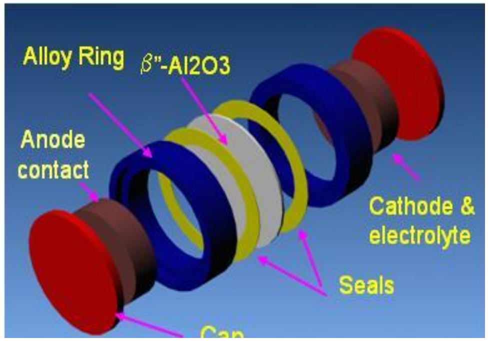
Planar Na-Beta Batteries Development for Renewable Integration and Grid Applications

Eagle-Picher/PNNL Path to Planar Na Battery

EaglePicher™ Technologies, LLC
An OMG Company

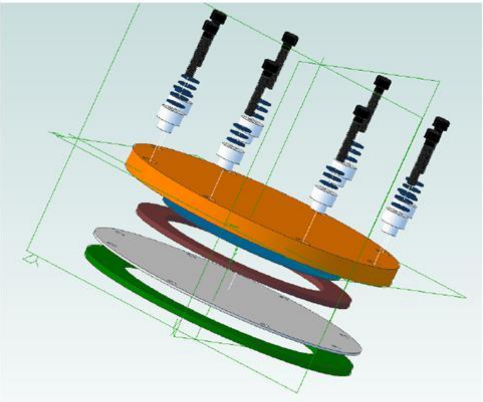
Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

3.0cm^2 Button Cell



Materials development and performance testing.

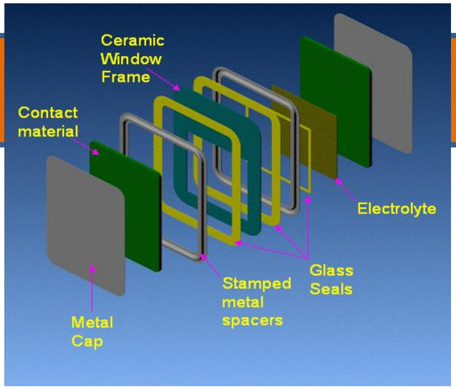
64cm^2
XL-Button Cell



Materials scale-up with large-scale performance and life testing.

- *3 year program to scale up and demonstrate planar Na-battery technology.*

Multicell
Planar Stack



Manufacturing friendly components and fabrication techniques.

200cm^2 Stack

Modular stack design with performance and life testing.

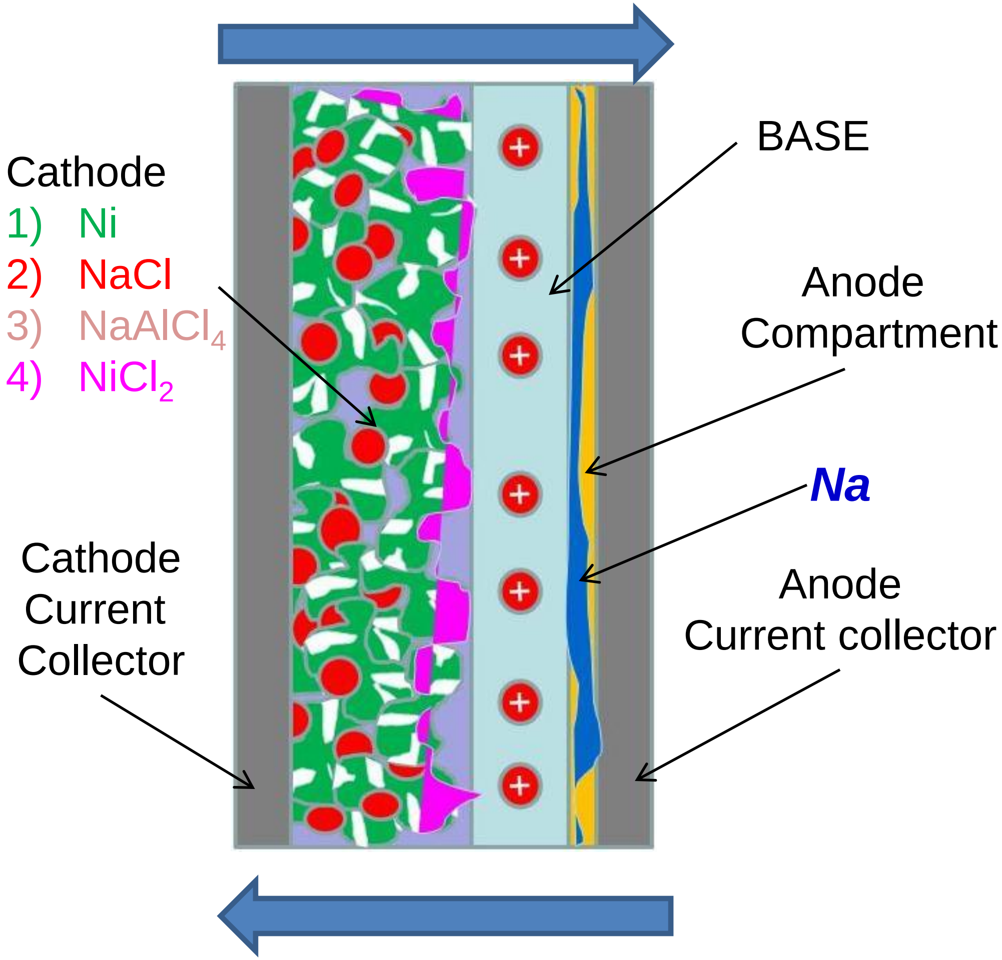
- *Tubular Na –Metal Halide chemistry demonstrated > 1000 cycles at high DOD.*
- *Decrease capital cost by moving to high volume planar manufacturing. Planar technology has higher volumetric power density than tubular architecture*
- *Increase cycle life by reduced temperature operation.*

arpa·e

Basic Na-$NiCl_2$ Battery Chemistry

Charging Reaction

$$2e^- + Ni + 2NaCl \rightarrow 2Na + NiCl_2$$



Discharging Reaction

$$2Na + NiCl_2 \rightarrow 2e^- + Ni + 2NaCl$$

Key elements

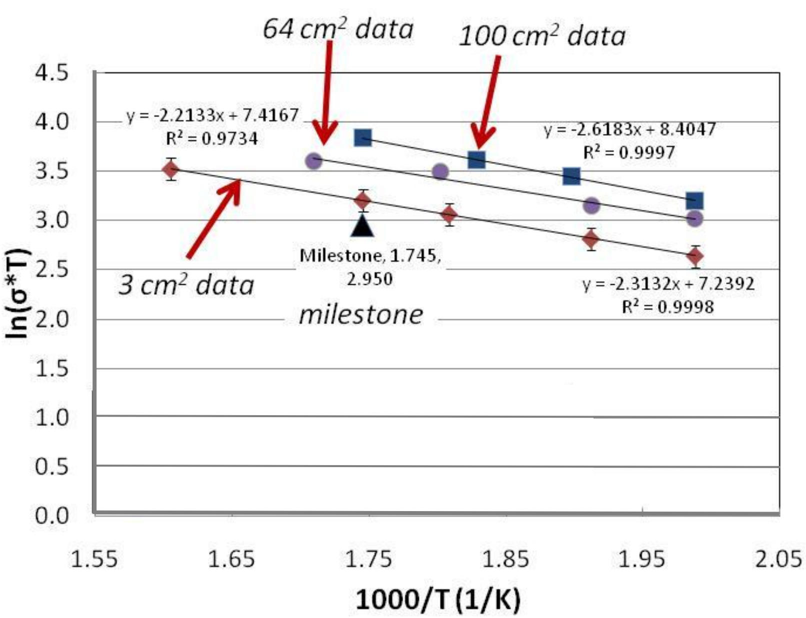
- 2.58 V OVC
- ~3.0 V cutoff voltage for charging
  - Increase R from $NiCl_2$
  - Melt degradation.
- 1.8 V cutoff on discharging
  - Al plating from melt
- Typically 20 – 80% SOC swing.

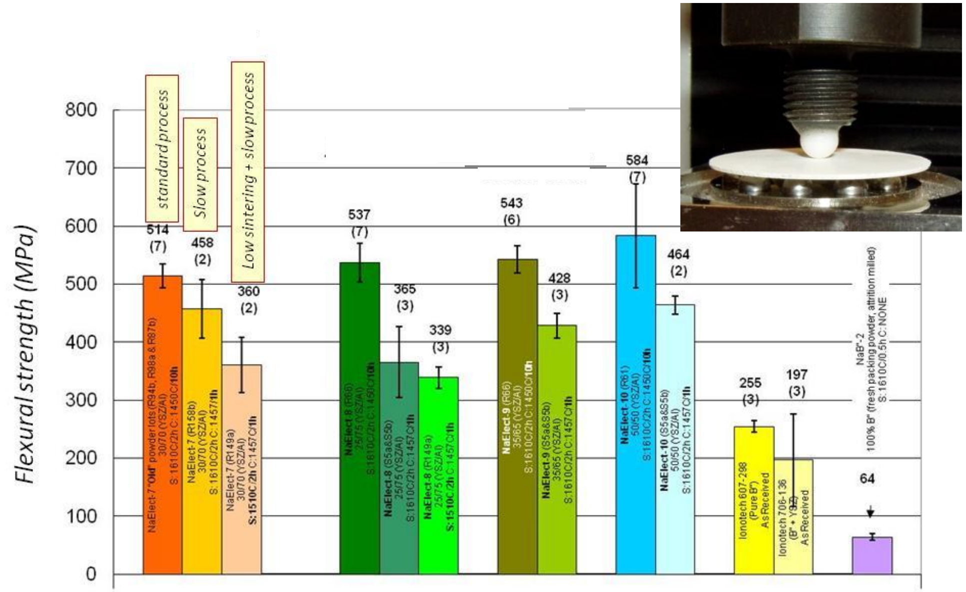
PNNL efforts focused on

- Scale-up of BASE fabrication process.
- Development of durable glass seals capable of withstanding melt
- Demonstrating larger scale 64 cm^2 cells
- Cathode chemistry development to improve durability at higher specific energy density.
- Transition technology to EP

BASE properties are function of fabrication, composition, and processing conditions.

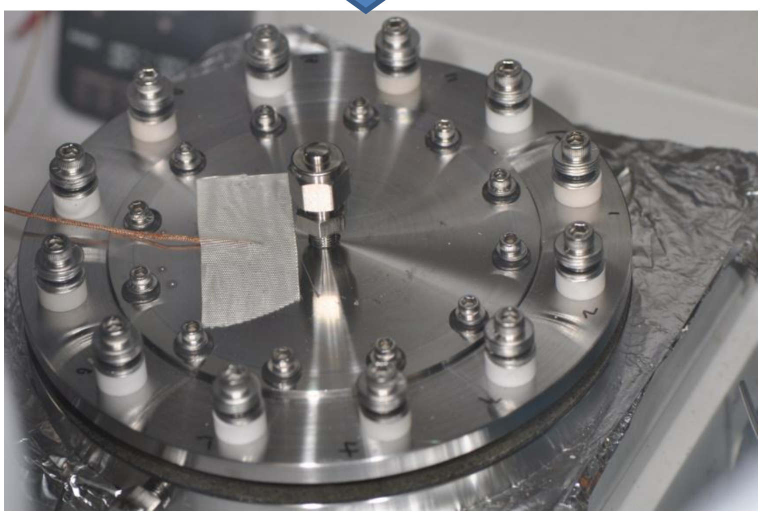
64 cm² BASE sample glass sealed to a alumina ring prior to application of electrodes and resistivity test.





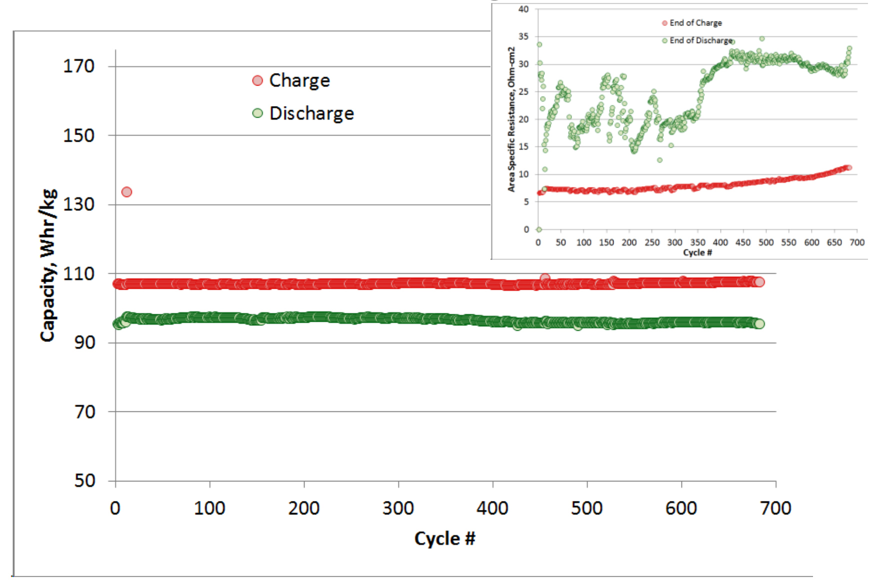
- *Critical to understand impact of process conditions on flexural strength and conductivity.*
- *Goal : Maintain > 0.03 S/cm at 300° C with RT flexural strength > 400 MPa flexural strength.*

Progress of 64 cm^2 cell

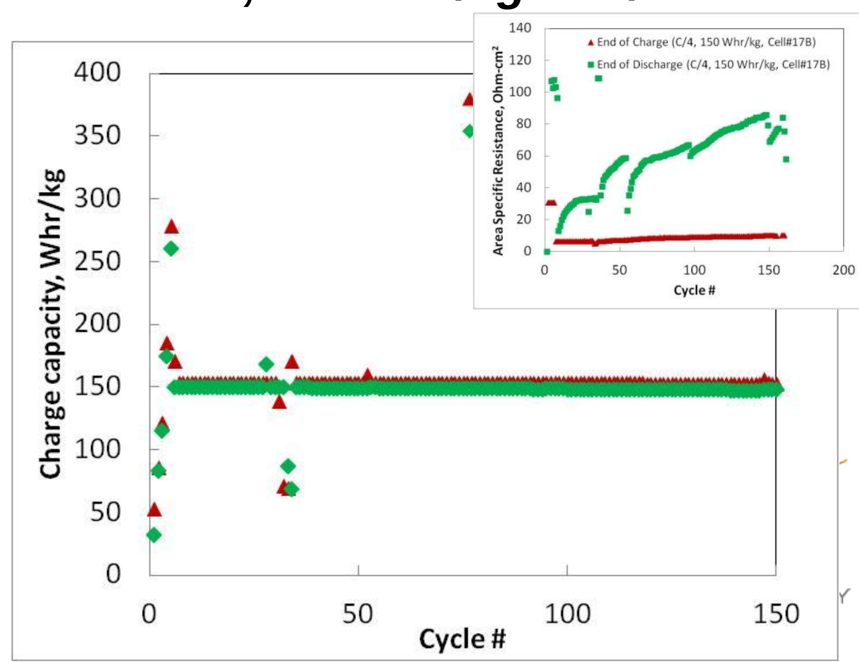


- *64cm^2 cell - 100whr/kg at 1C - 91% efficiency - 280°C for over 700 cycles*
- *No capacity fade for first 800 cycles .*

64cm^2 cell, 100 Whr/kg at 1C - 280°C

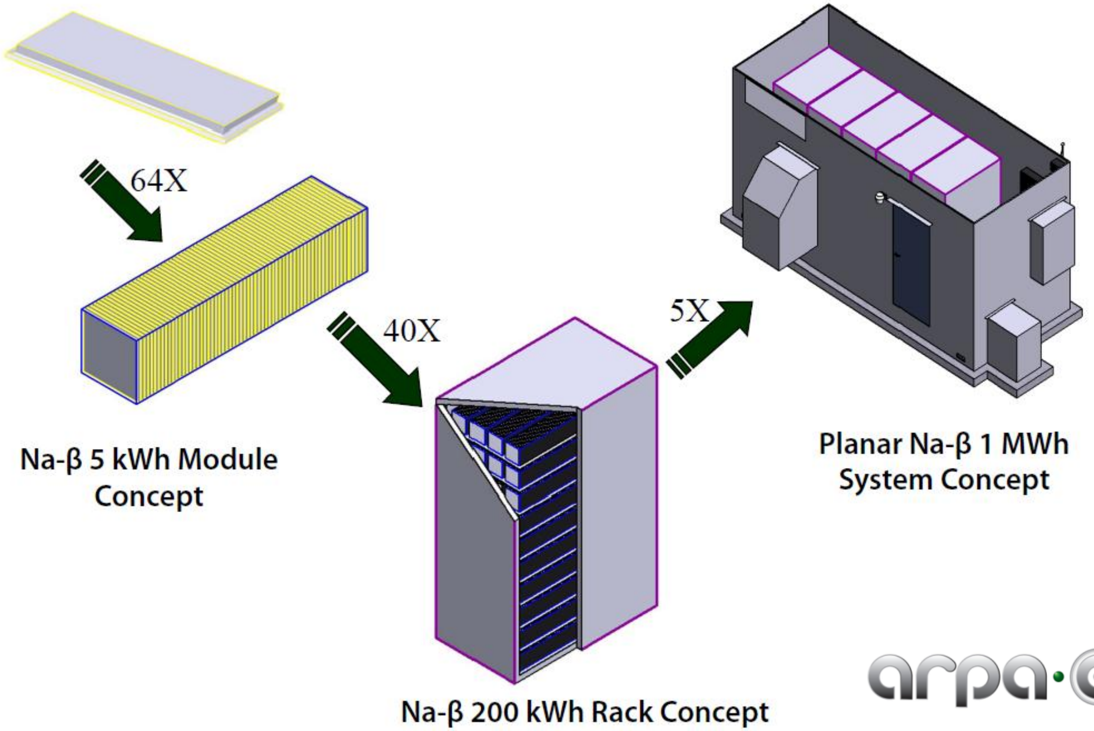


64cm^2 cell, 150 Whr/kg at C/4 - 280°C

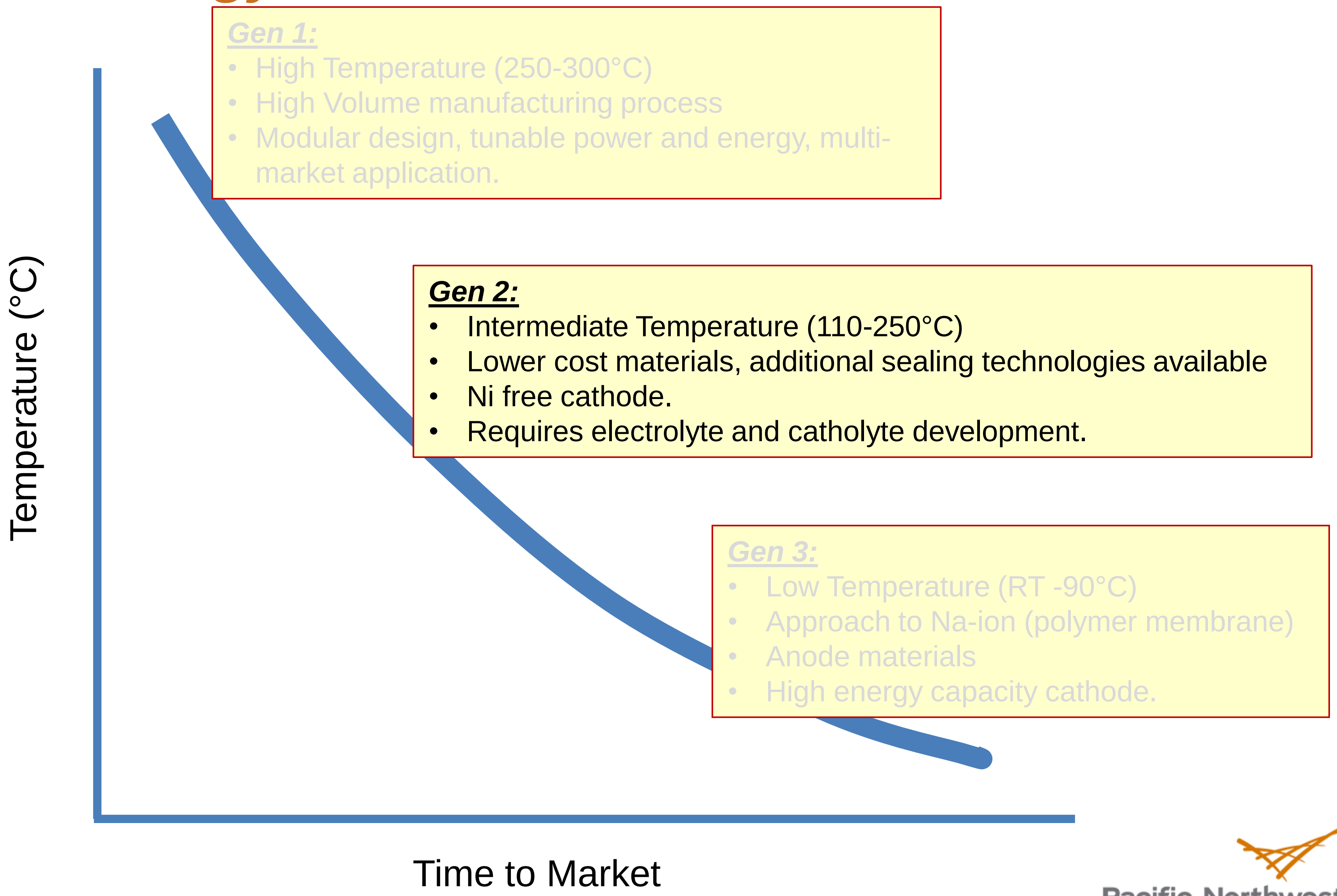


EaglePicher – PNNL Next Steps

- *Assemble and test multicell 64 cm^2 stack – 150 Whr/kg of active cathode*
- *1000 hrs durability of seal*
- *Larger scale cells running at 200 Whr/kg of active cathode.*
- *5 kW module*



Intermediate Temperature Sodium Battery Technology



Pacific Northwest NATIONAL LABORATORY

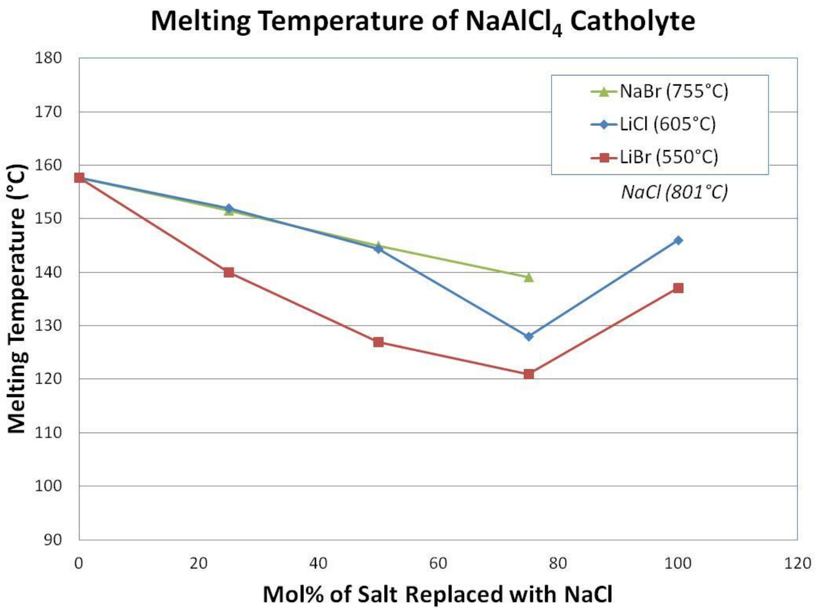
FY11 Intermediate Temperature (110-250℃) Na-Metal Halide Battery Research Plan

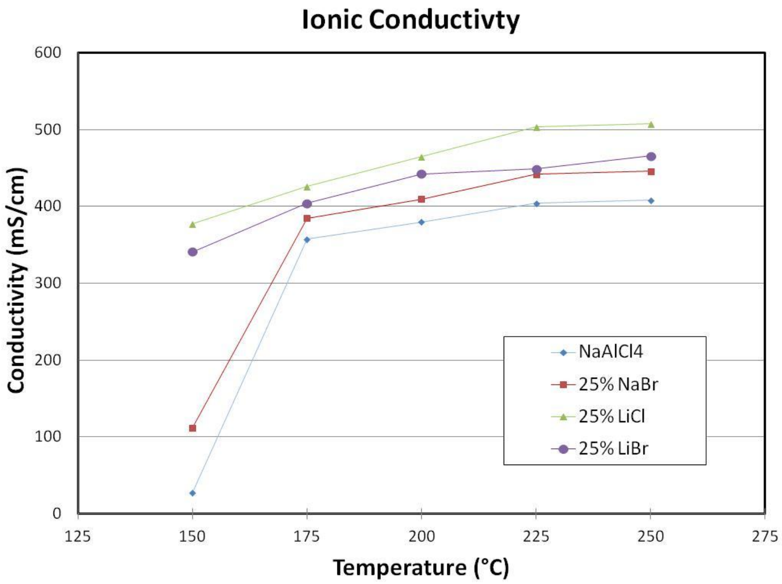
- **Goal: To demonstrate Na- metal halide battery operated at ≤ 200°C**
  - ***64 cm^2 cell with comparable performance compared to current cells operated at 280℃***

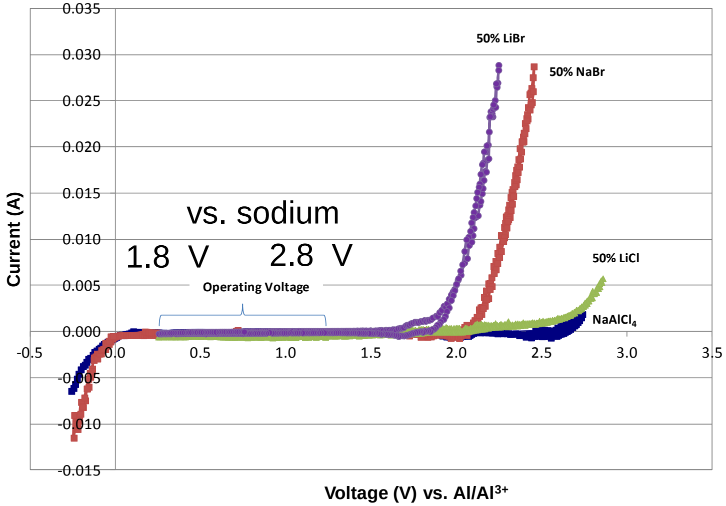
- **Technical Challenges**
  - ***Catholyte and Cathode Chemistry***
  - ***Low-resistance BASE***
  - ***Na wetting at lower temperatures***
  - ***Seal and new cell design***

Pacific Northwest
NATIONAL LABORATORY

Low Temperature Catholyte Development







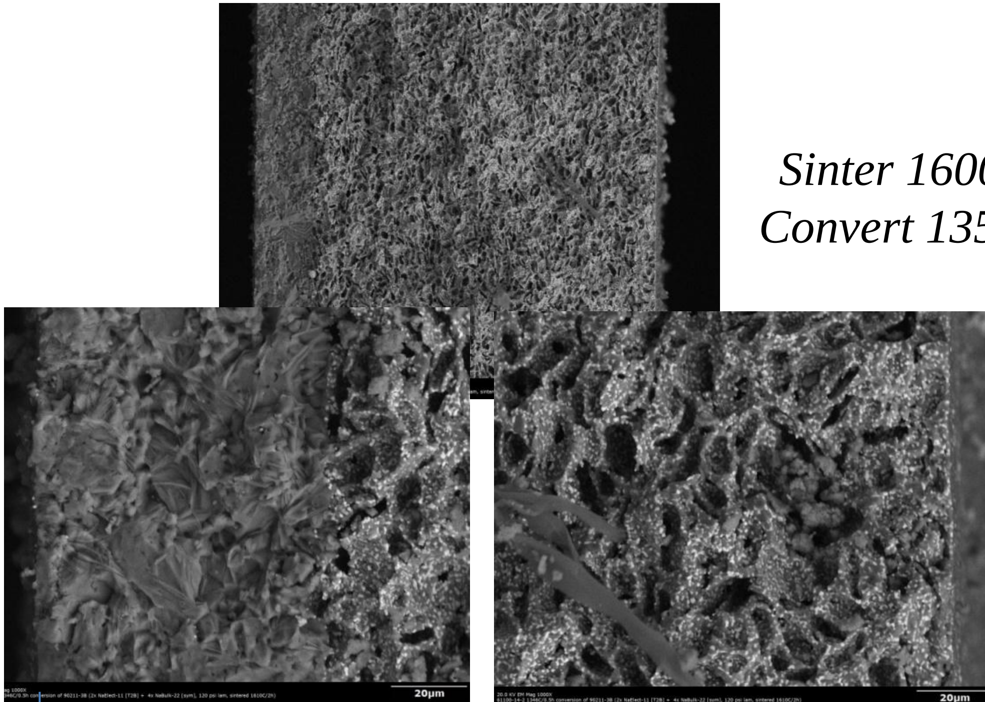
Additions to $NaAlCl_4$

- Decrease T_m of catholyte by 20 - 40°C
- High ionic conductivity < 200°C with ≥ 25% salt replacement.
- Does not impact electrochemical stability of catholyte.

Pacific Northwest NATIONAL LABORATORY

Low Temperature BASE Development

Sinter 1600°C
Convert 1350°C

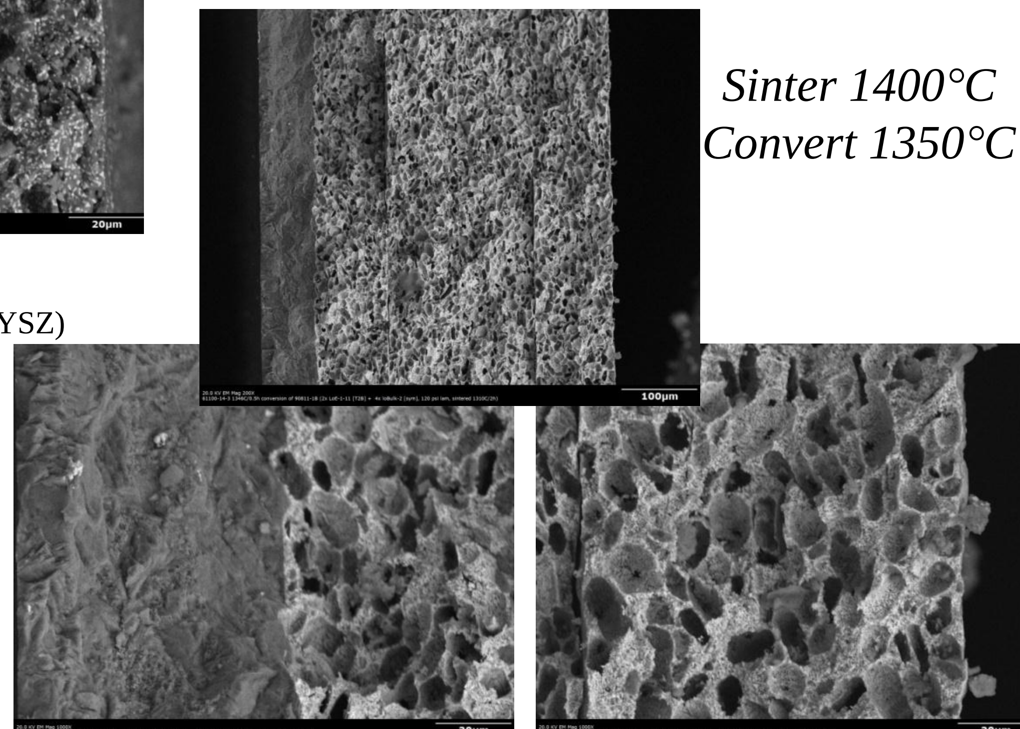


Electrolyte –
50 µm - (100% β”)

Porous Electrode
~400µm (70/30 β” – YSZ)

- Goal is to minimize electrolyte resistance while retaining sufficient strength for larger scale planar batteries.
- 50 µm β” electrolyte on porous support
- Currently focused on determining strength – porosity relationship.

Sinter 1400°C
Convert 1350°C

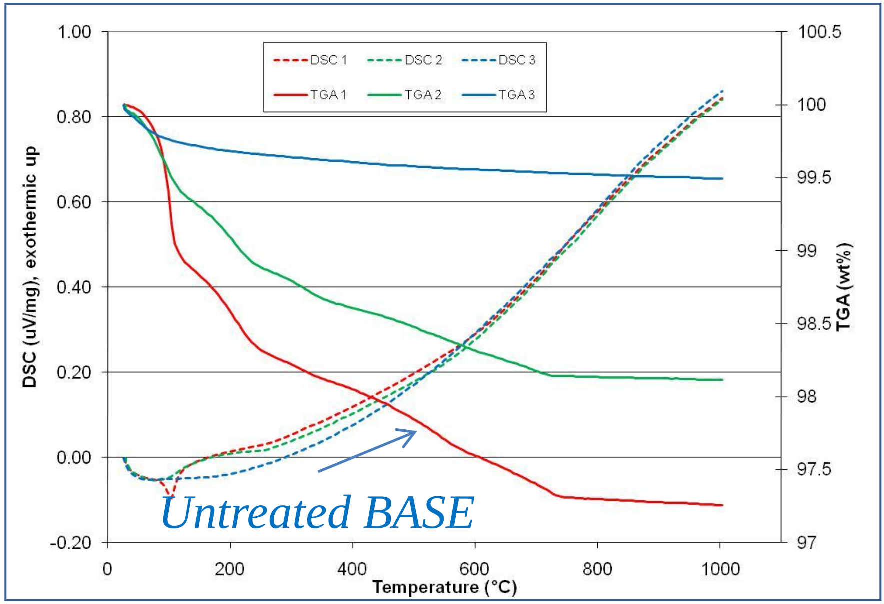


Electrolyte –
50 µm - (100% β”)

Porous Electrode
~400µm (70/30 YSZ - β”)

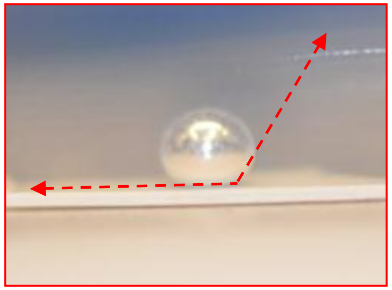
Low Temperature Na wetting

- As-prepared BASE shows extensive hydration after exposure to air. Wetting angle > 90° for all temperatures studied and poor adherence.
- Vacuum treated BASE shows improved wetting and adherence
- Wetting angle > 130° at 250°C - significant issues for low temperature operation?



Na drop showed no adherence to β" surface
→ Na rolled off surface
θ ~ 180°

T = 250°C

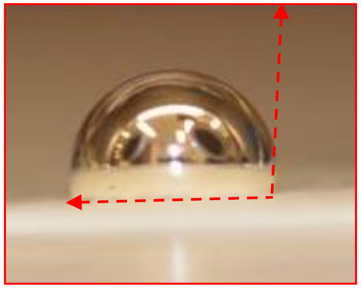


θ ~ 130°

Treated BASE
425°C – 60 hr vacuum

Na drop showed no adherence to β" surface
→ Na rolled off surface
θ ~ 180°

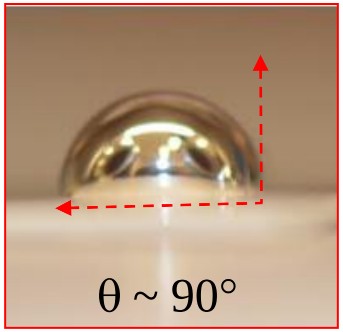
T = 300°C

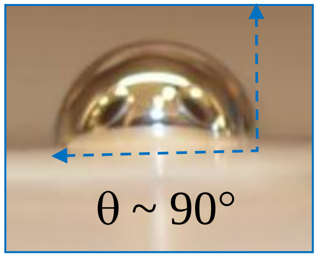


θ ~ 100°

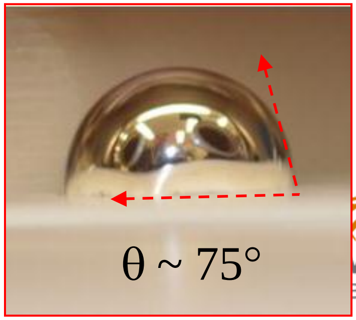
Na drop showed no adherence to β" surface
→ Na rolled off surface
θ ~ 180°

T = 325°C



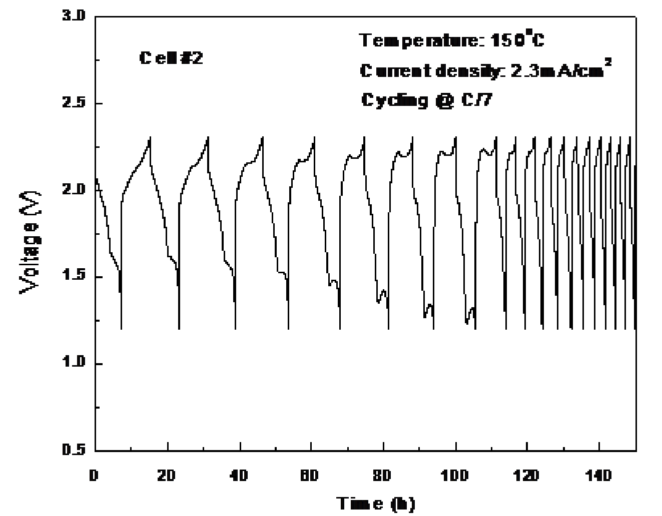


T = 350°C



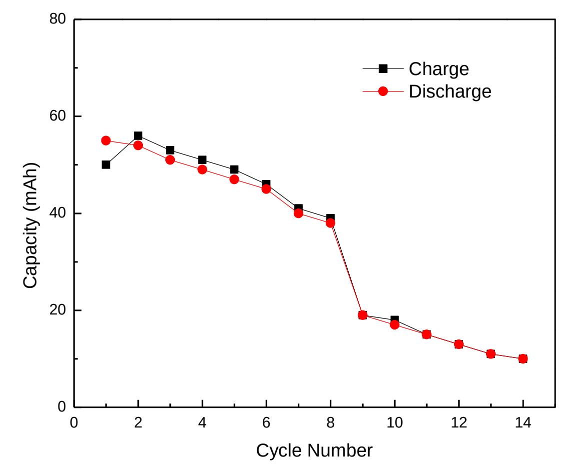
Intermediate Temperature Na-S

- ***Goal:*** Develop 150 – 200°C temperature Na – S battery which can:
  - Less corrosive environment
  - Built in discharge state and charged on site
  - Can withstand multiple freeze/thaw cycles.



Sulfur Solubility in Various Organic Solvents (wt.%)

	Boiling point (°C)	25°C	50°C	100°C	150°C	200°C
tri(ethylene glycol) dimethyl ether	216	------	0.5	2.5	7.0	-------
tetra(ethylene glycol) dimethyl ether	275	0.16	1.01	3.0	7.0	-------
di(ethylene glycol) dibutyl ether	256	-------	--------	0.5	1.5	-------
Dimethylaniline	194	3.37	6.92	38.4	------	-------
propylene carbonate	242	------	------	------	------	-------
ethylene carbonate	244	------	------	------	------	------

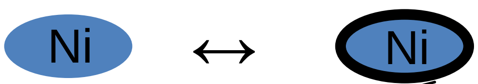


Na-Metal Halide Concepts (non-Ni)

➢ Goal: Replace highest cost material component(Ni) with lower cost metals with improved performance.

ZEBRA type chemistry: insoluble MH

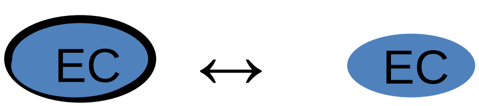
$Ni + 2NaCl \rightarrow 2Na + NiCl_2$ (charge)
$NiCl_2 + 2Na \rightarrow 2NaCl + Ni$ (discharge)



$NiCl_2$ (insoluble)

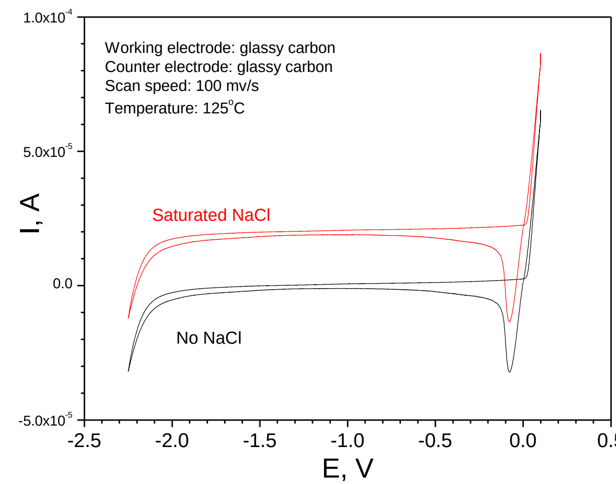
Metal coated chemistry: soluble MH

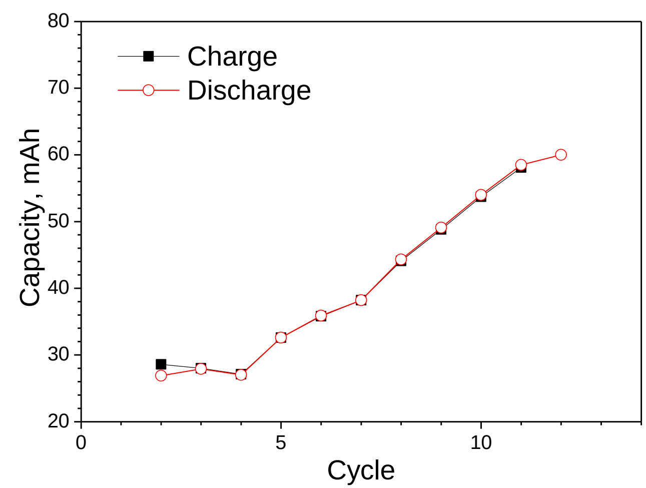
$EC/M_x + NaCl \rightarrow Na + M_xCl_y + EC$ (c)
$EC + M_xCl_y + Na \rightarrow NaCl + EC/Mx$ (d)



M_x Coated

M_xCl_y (soluble)



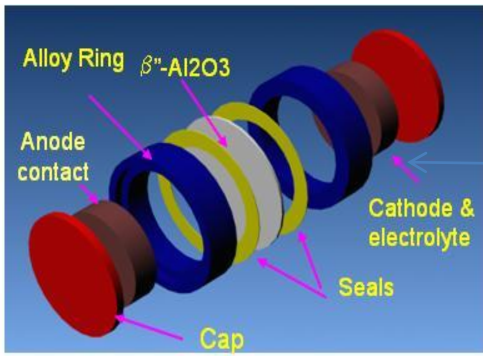


Internal DOE EED LDRD Funded FY2010, J. Lemmon, G. Li and X. Lu

Intermediate Temperature Na-Air with BASE

Goal: Improve performance, low cost alkali metal – air.
Path: Improve solubility of Na_xO_y products in cathode with higher temperature.

3.0cm^2 Button Cell



Replace metal cathode with temperature stable air cathode.

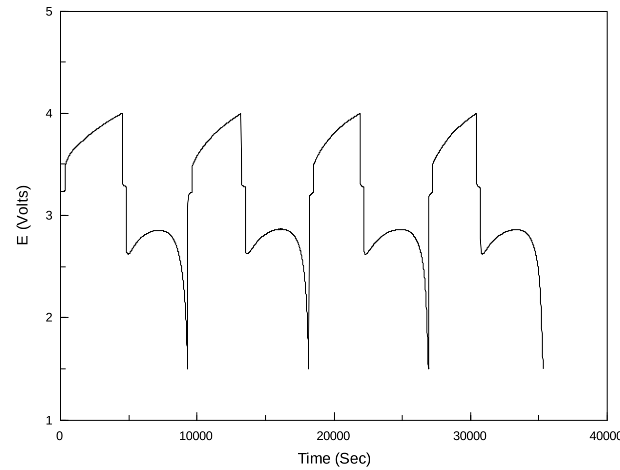
Cell Characteristics:

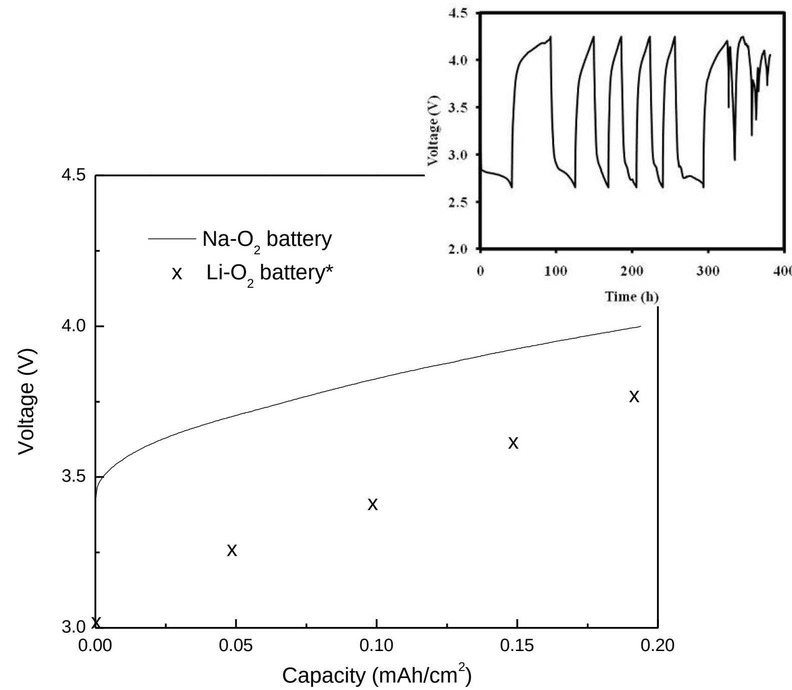
Temperature: 140°C
OCV: 3.2V vs Na
Current: 0.15mA/cm^2.

Summary:

- High IR from BASE electrolyte.
- Cycled in air, capacity decreases.
- Overpotential on charge higher than Li.
- Overpotential increase rate lower than Li.

Na-Air Low rate cycling





* J. Xiao, et al., J. Power Sources 196 (2011) 5674.

Acknowledgements

- **ARPA-e DOE Award Number: DE-AR0000045**
  - *Dr. Mark Johnson, Dr. Dave Danielson*
- **DOE-OE Energy Storage Program,**
  - *Dr. Imre Gyuk*
- **PNNL internal LDRD Funding**

Pacific Northwest
NATIONAL LABORATORY